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**OAK RIDGE
NATIONAL
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**Mercury Assessment
for Water and Sediment in
Oak Ridge National Laboratory Streams**

Fred G. Taylor, Jr.

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Authors: F. G. Taylor, Jr.

Abstract: This report identifies sources of mercury from past operations and spills and reports data from monitoring and sampling stations set up based on knowledge of mercury discharges from pipes to streams, and a review of chemical data from previous studies. This study was designed to assess the potential for metal reach surrounding streams and rivers.

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MERCURY ASSESSMENT FOR WATER AND SEDIMENT IN
OAK RIDGE NATIONAL LABORATORY STREAMS

Fred G. Taylor, Jr.

Environmental and Health Protection Division

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1.0 INTRODUCTION

An assessment plan was implemented in compliance with the Clean Water Act and the Oak Ridge National Laboratory's (ORNL) National Pollutant Discharge Elimination System (NPDES) permit to identify, locate, and minimize all sources of mercury contamination in ORNL discharges to the aquatic environment. This plan was designed to identify sources of mercury from past operations and spills through a review of file records and personal interviews. A network of monitoring and sampling stations, based on knowledge of mercury deposits in receiving streams, knowledge of mercury discharges from pipes to streams, and a review of chemical data from previous contaminant surveys, was established for sample collection. The plan was designed to assess the potential for the metal reaching surrounding streams and rivers by placement of sampling sites relative to potential contaminant movement from areas of deposition. This summary report describes appropriate sampling and analytical procedures, defines the database management system, provides for chain-of-custody, Quality Assurance (QA), and presents contaminant concentration data for 1988.

2.0 AREA RECEIVING WATERS

Effluents from the numerous laboratories at ORNL are treated and subsequently monitored before discharging into the receiving streams at permissible concentrations. In previous years, before stringent regulations, some contaminants reached various streams primarily as the result of accidental spills and leakages. The intent of this effort is to identify sources or pools of a single heavy metal (mercury) and to characterize the extent and the specific locations of contamination. A summary of area receiving streams or bodies of water is provided with a brief description of potential contaminant sources.

2.1 CLINCH RIVER-MELTON HILL LAKE

This body of water receives discharge from two holding ponds in the Fuel Recycle area. These ponds are categorized as Category I (storm water) and Category II (cooling tower discharge) outfalls.

2.2 CLINCH RIVER-WATTS BAR LAKE

Downstream from Melton Hill Dam, the Clinch River-Watts Bar Lake receives all the wastewater discharge from ORNL with the exception of that from the two holding ponds listed in the above paragraph.

2.3 WHITE OAK CREEK

This perennial stream enters north of the ORNL site from Chestnut Ridge and runs along the main Bethel Valley complex collecting discharges from Category I, II, and III outfalls; miscellaneous source outfalls; and

point source outfalls X01, X02, X04, X06, X07, and X11. Fifth Creek, First Creek, and Northwest Tributary join White Oak Creek in Bethel Valley and Melton Branch joins White Oak Creek in Melton Valley.

2.4 FIFTH CREEK

This small stream originates from springs at the base of Chestnut Ridge and enters the north side of the ORNL main complex in Bethel Valley and receives discharges from Category I, II, and III outfalls. At the south end of the ORNL site Fifth Creek joins White Oak Creek.

2.5 FIRST CREEK

This stream originates from springs near the base of Chestnut Ridge and enters the north side of the ORNL main complex in Bethel Valley where it receives discharges from Category I, II, and III outfalls. First Creek is joined by Northwest Tributary at the south end of the ORNL site and enters White Oak Creek.

2.6 NORTHWEST TRIBUTARY

This stream originates primarily from springs near the base of Haw Ridge and enters the west side of the ORNL complex in Bethel Valley where it receives discharge from the X03 point source outfall. Northwest Tributary joins First Creek before entering White Oak Creek.

2.7 MELTON BRANCH

Several small springs from Haw and Copper Ridges combine to form Melton Branch. Melton Branch enters the east side of Melton Valley where it receives discharges from Category I, II, and III outfalls and point source outfalls X08 and X09. Melton Branch joins White Oak Creek approximately 0.5 km (0.3 mile) above White Oak Lake.

2.8 WHITE OAK LAKE

This impoundment serves as the last monitoring point and holding basin for wastewater discharges leaving ORNL. No outfalls discharge directly into the lake.

3.0 MERCURY SOURCES (SPILLS)

Two major uses of mercury at ORNL involved pilot plant operations in 1954-55 supporting the thermonuclear weapons program at Y-12. Both activities involved separation processes in Buildings 4501 and 4505. At the time of the operations, an unknown number of mercury spills occurred. Although these spills were cleaned up, it is evident from soil analyses around the buildings that quantities of mercury escaped and reached the environment (Oakes, 1983a,b). Key individuals with personal knowledge of the operations were interviewed concerning the history of mercury spills.

A summary is provided of each process with estimates of mercury lost through operational procedures, and included with additional reportable incidents in Table 1.

Table 1. Summary of known mercury spills at ORNL

Building	Process	Year	Amount	Outfall
4501	Lithium isotope separation	1954	>23,000 kg	362,363
4505	Uranium and thorium metal production	1955	2,000 kg	362,363
3592	Mercury cleaning	1963	5,000 kg	207
3503	Mercury flask and clean mercury storage	1963	unknown	207
2525	Spill	1981	1.5 kg	103,207, 208
4500S	Spill	1980	<1.0 kg	109,217, 218,311
3500	Spill	1981	<0.02 kg	163,162, 261,361, 207

3.1 BUILDING 4505, EXPERIMENTAL ENGINEERING LABORATORY

A process termed METALLEX was demonstrated in 1955 in Building 4505 to illustrate the production of uranium and thorium metals by reducing UCl_4 or $ThCl_4$ using sodium amalgam. The amalgam was pressed to form a billet and the billet was sintered to remove the mercury by vacuum distillation leaving the uranium or thorium metal. An early report indicated as much as 134,608 kg (296,139 lb) of mercury were required as materials for the process. Personnel involved in the project estimate that 2000 kg (4400 lb) may have been lost in spills (Dinsmore, 1986). Soil analyses near the building confirm mercury contamination (Oakes, 1983b).

3.2 BUILDING 4501, HIGH-LEVEL RADIOCHEMICAL LABORATORY

The OREX process was similar to the METALLEX procedure but was designed to separate lithium isotopes. The lithium was amalgamated, pressed into billets, sintered, and the mercury removed by vacuum

distillation leaving the lithium. This process was carried out in the basement of Building 4501 in 1954. The basement floor was of concrete construction with tar seams and was flooded with 10 cm (4 in) of water. The water layer was intended to reduce mercury fumes in the building atmosphere. A steel grate above the water pool supported equipment and personnel. Throughout the process some mercury escaped from the basement at the tar seams as is confirmed by soil analyses (Oakes, 1983b). The condensed mercury was pumped to a tank truck where it was transferred to Building 3592 for cleaning and recycle. It has been estimated that an excess of 22,680 kg (50,000 lb) of mercury may have been lost during the process (Parker, 1986). Most spills were associated with pump failures where amalgam was being pumped from the basement to the upper level of Building 4501.

3.3 BUILDING 3592, UNIT OPERATIONS VOLATILITY LABORATORY

Mercury distilled from the OREX process was transported to Building 3592 for cleaning by resin exchange columns. Following cleaning, it was placed in containers and later removed to Y-12. A spill occurred due to operator error which involved 400 gal (20,500 kg) of mercury. Approximately 300-350 gal were recovered by vacuum sweeping. The remainder, 50-100 gal (2500 to 5000 kg), was lost to the surrounding soil, subject to transport to White Oak Creek through the Laboratory storm drain system (Dinsmore, 1986). Soil and sediment analyses confirm contamination by mercury (Oakes, 1983a).

3.4 BUILDING 3503, HIGH RADIATION CHEMICAL ENGINEERING LABORATORY

Building 3503 was used to store empty mercury flasks and cleaned mercury from the resin columns of Building 3592. By 1963 all the materials associated with METALLEX and OREX had been removed to Y-12. Some small quantity of mercury may have reached White Oak Creek through the Laboratory storm drainage system. No estimate is available of the amount spilled in Building 3503. Analyses of the Building 3503 storage area confirm that mercury had escaped the building (Oakes, 1983a).

3.5 BUILDING 2525, PLANT AND EQUIPMENT FABRICATION SHOP

In May of 1981, mercury was reported in the drain system from Building 2525. The origin of the spill was reported as unknown. Less than 1.5 kg (3 lb) were removed by vacuum cleaning and submitted for cleanup and recycle (Eisenhower, 1981; Kelly and Eisenhower, 1982).

3.6 BUILDING 4500S, CENTRAL RESEARCH COMPLEX

Two minor spills are recorded (Kelly and Eisenhower, 1982) from laboratories in the Central Research Complex (Building 4500S) during 1980. The quantities were noted as a trace (<10 g) and 100 g. One spill was noted as operator error and the other as mechanical failure. In both cases there was no mention of the action taken.

3.7 BUILDING 3500, INSTRUMENTATION AND CONTROLS

An undisclosed quantity of mercury was reported as a spill in 1981. Kelly and Eisenhower (1982) indicated it was a "puddle" (10 to 20 g) and resulted from operator error.

4.0 SAMPLE LOCATIONS

As a means of establishing baseline data for environmental concentrations of mercury, water was collected from receiving streams near the various Laboratory outfalls. Areas sampled included selected Category I, II, and III outfalls; NPDES Serial Numbered Sampling sites; and areas surrounding known mercury spills. Category I outfalls receive water from storm drains. Those outfalls sampled are identified in Table 2 and were selected on the basis of the potential for water transport from areas near buildings with a past history of mercury concern. Category II outfalls (Table 3) include storage area drains, spill area drains, roof and parking lot drains, and cooling tower blowdown and condensate drains. Although the potential for mercury entering these systems is minimal, several outfalls were identified for sampling. Category III outfalls receive routine process wastes and periodic laboratory wastes. These systems represent the greatest potential for mercury transport to receiving streams. Outfalls sampled are identified in Table 4. The Serial Numbered Sampling sites routinely sampled for radiological contaminants (Table 5) are included to provide a broader survey for mercury in the Laboratory's receiving streams.

Table 2. Candidate Category I sampling stations
by outfall number and receiving stream

WHITE OAK CREEK

Outfalls: 101, 103, 106, 109, 116

FIRST CREEK

Outfalls: 141, 142, 143

FIFTH CREEK

Outfalls: 161, 162, 163, 164

MELTON BRANCH

Outfall: 181

Table 3. Candidate Category II sampling stations^a
by outfall number and receiving stream

WHITE OAK CREEK

Parking Lot Runoff: 202, 204, 207, 208, 210,
218, 222, 223, 230, 232,
233, 234

Condensate: 217

Cooling Tower Blowdown: 216

Spill Area Drain: 206

FIRST CREEK

Parking Lot Runoff: 241, 243, 247, 248,

Storage Area Drain: 244, 246

MELTON BRANCH

Parking Lot Runoff: 283

Cooling Tower Blowdown: 281

FIFTH CREEK

Parking Lot Runoff: 265

Condensate: 261, 262

Cooling Tower Blowdown: 268

^aRoof drains, parking lot drains, storage area
drains, spill area drains, once-through cooling
water, cooling tower blowdown and condensate

Table 4. Candidate Category III sampling stations (process or laboratory drains) by outfall number and receiving system

WHITE OAK CREEK

Process Drains: 301, 302, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314

FIFTH CREEK

Process Drains: 361, 362, 363, 364, 365, 366, 367, 368

MELTON BRANCH

Settling Ponds: 381, 382, 384, 385, 386

FIRST CREEK

Process Drains: 341, 342, 343, 344

Table 5. Candidate serial numbered outfalls (point sources) and receiving streams

White Oak Creek:	X01 - Sewage Treatment Plant, X02 - Coal Yard Runoff, X04 - 2000 Area, X06 - 190 Process Ponds, X07 - Process Waste Treatment, X11 - Acid Neutralization Facility
First Creek:	X12 - NRWTF
Melton Branch:	X08 - TRU, 7907 and 7908 Ponds, X09 - HFIR, 7905 and 7906 Ponds
Northwest Tributary:	X03 - 1500 Area Pit

Several additional sites which are routinely sampled for other contaminants are included in the sampling design. These are White Oak Dam, White Oak Creek, Headwaters of White Oak Creek, Melton Hill Dam, Melton Branch, Headwaters of Melton Branch, 7500 Bridge (White Oak Creek), and the White Oak Creek Flume south of Waste Basins 3539 and 3540.

A total of 90 sites (Table 6) were available for sampling (water) during the survey with an additional 12 sites for sediment samples. Sampling sites in the ORNL Bethel Valley complex are noted in Fig. 1, while sites in the Melton Valley area are illustrated in Fig. 2. In a preliminary survey (1987), 74 sites (222 analyses) were sampled for water analyses, in comparison to 61 sites (183 analyses) in February 1988; 88 sites (264 analyses) were sampled in October 1988. An additional 12 sites (36 analyses) were sampled in October 1988 for mercury contamination of sediments. Most sites were sampled twice during the year and consisted of three replicate samples for each site. The sampling periods were selected to represent periods of soil moisture recharge and soil water deficit. Sediment samples were primarily from Fifth Creek in the vicinity of suspected mercury deposition, White Oak Creek, and White Oak Creek headwaters.

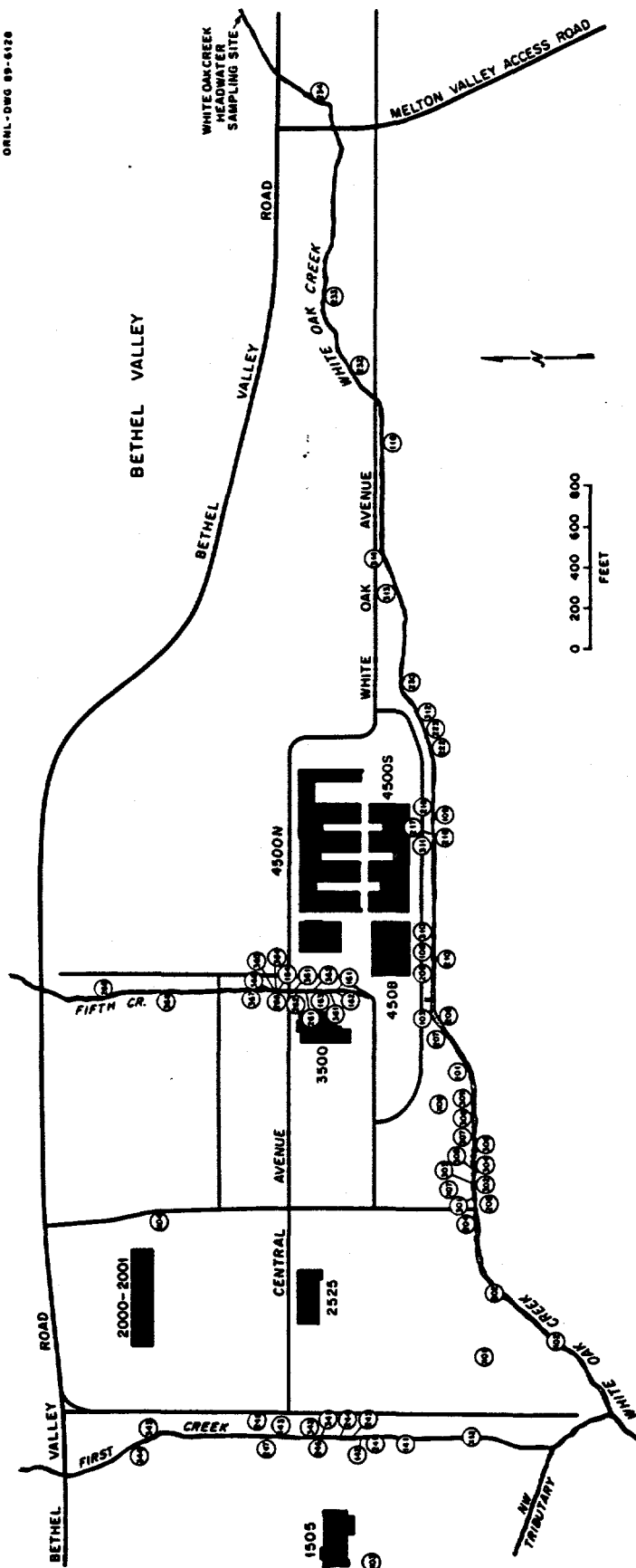


Fig. 1. Sampling stations in the ORNL Bethel Valley complex. The circled numbers are positioned as near as possible to the outfall. Series Number (100, 200, 300, or X) corresponds to the outfall categories identified in Tables 2-6.

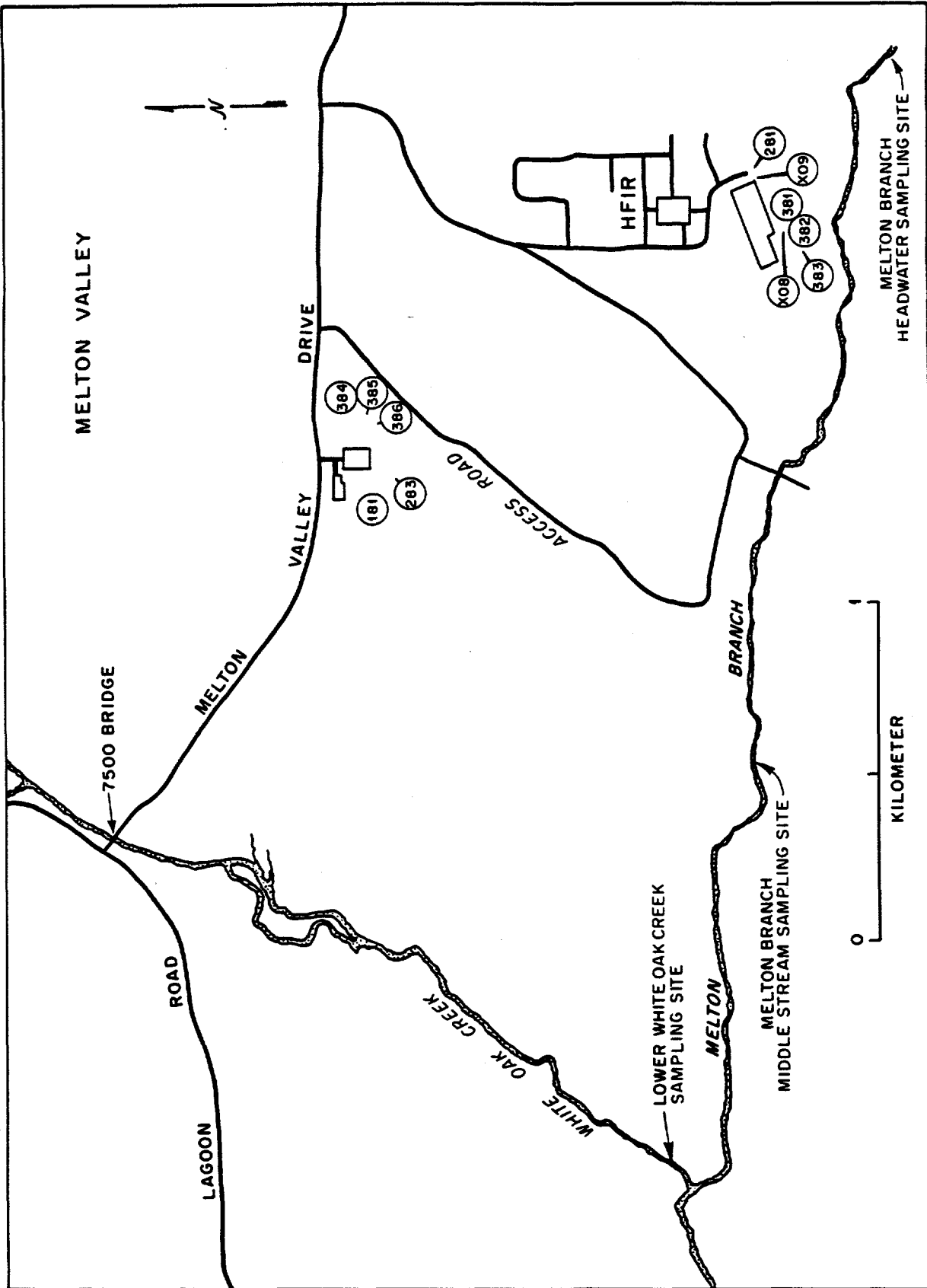


Fig. 2. Sampling stations in the ORNL Melton Valley complex. The circled numbers are positioned as near as possible to the outfall. Series number (100, 200, 300, or X) corresponds to the outfall categories identified in Tables 2-6.

Table 6. Summary of receiving waters outfall identifiers (number) and miscellaneous locations for mercury determinations^a

Receiving water	Outfall or area to be sampled
White Oak Creek	101, 103, 106, 109, 116, 202, 204, 206, 207, 208, 209, 210, 216, 217, 218, 222, 223, 230, 232, 233, 234, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, X01, X02, X04, X06, X07, 7500 B, flume, headwaters, lower creek section, White Oak Dam
First Creek	141, 142, 143, 241, 243, 244, 246, 247, 248, 341, 342, 343, 344, X12
Fifth Creek:	161, 162, 163, 164, 261, 262, 265, 268, 361, 362, 363, 364, 365, 366, 367, 368
Melton Branch:	181, 281, 283, 381, 382, 383, 384, 385, 386, X08, X09, headwaters section, middle branch section, and Melton Hill Dam
Northwest Tributary	X03

^aThe actual number of outfalls sampled varied between sampling periods because some outfalls had no discharge.

5.0 SAMPLE COLLECTION

All water samples consisted of three replicate, manual grab samples collected during two sampling periods (dry and wet seasons) in 1988. Samples were collected in 1-L I-Chem high-density polyethylene bottles with teflon caps. I-Chem bottles are proprietary containers, precleaned by the vendor to EPA specifications where microdeterminations are requested. Samples were preserved immediately upon collection by acidifying with concentrated nitric acid to a pH of <2.0. Sediment samples were collected at selected stations and placed in glass containers. The glass containers were also I-Chem, EPA approved. Generally, samples were analyzed as soon as possible after collection, and no sample analysis exceeded the maximum allowable holding time of 28 days.

6.0 SAMPLE PROCEDURES, DATA MANAGEMENT, AND CONTROL

6.1 ANALYTICAL METHODS

Water and sediment samples were analyzed for total mercury content by manual cold vapor atomic absorption (USEPA, 1982). A modification of Method 245.1 (USEPA, 1983) was utilized for all analyses, and the results of sediment analyses were reported on a dry weight basis.

6.2 DATABASE MANAGEMENT SYSTEM

A computerized NPDES database exists on the Environmental Monitoring and Compliance Section's VAX computer. The database can be modified to maintain all records and allow for retrieval of records and data from all sampling and monitoring activities. The database permits tracking of all sampling sites and includes the date and time of collection, the identity of the individuals collecting each sample, and a description of how and under what conditions the sample was taken. Analytical data are transferred to the database by computer from entries verified by the laboratory supervisor in the Analytical Chemistry Division's computer. Hard copies also provide verification. The structure of the database is such that retrieval of information for risk assessment is possible.

6.3 QUALITY ASSURANCE

6.3.1 Sample Analysis

The validity of the sample analysis was demonstrated by the use of distilled water blanks to ensure that all glassware and reagents were interference-free. The blanks were carried through all stages of sample preparation and analysis. Blanks were used with each set of samples. All samples were analyzed within the prescribed time limits (28 days) noted previously.

6.3.2 Replicate Samples

Three replicate field samples were collected to ensure that sampling techniques were consistent and to identify the concentration variability at each station. Laboratory duplicates within samples were analyzed to assure precision of analysis.

6.3.3 Chain-of-Custody

A "DOE X-10 Plant Chain-of-Custody" form was completed and remained with the sample until the Analytical Chemistry Division assumed control of the sample. At that time, an "Analytical Chemistry Division Chain-of-Custody" form was initiated and remained with the sample until the analyses were completed. Any additional information or variation in standard procedures was noted in a laboratory notebook.

7.0 RESULTS

The analytical chemistry data (1987) were used to identify areas of elevated mercury concentrations and were combined with maps of drainage systems to form the basis of the sampling program. The key objective of the sampling effort is to assist management in reducing mercury discharges from identifiable sources and to provide a means to monitor the effectiveness of any prescribed remedial procedures through subsequent sampling and analysis.

7.1 SCOPING SURVEY 1987 (WATER)

The sampling stations in this study were not sited to illustrate a concentration gradient from the ORNL complex, but rather to identify those areas of suspected mercury sources. Concentration data for water are expressed in ng/mL (ppb), while data for sediment are reported in ug/g, dry weight (ppm). Data from the 1987 scoping survey identified four locations with evidence of elevated mercury concentrations. Two hundred and twenty-two samples were analyzed for 74 stations (Table 7). The headwaters of White Oak Creek served as the background concentration. Analytical data indicated a concentration of <0.5 ng/mL ($n=3$). The highest concentration identified along White Oak Creek was near Outfall 309, which receives discharges from Building 4500, the Central Research Complex, through Holding Basins 3539 and 3540. These basins have been in operation since 1964. The mean concentration near the Outfall 309 was 2.27 ± 0.38 ng/mL. Serial Numbered Outfall X06 is the NPDES monitoring station serving Basins 3539 and 3540 and is approximately 100 m from White Oak Creek. Discharge from X06 flows to the creek through Outfall 309. The mean concentration for X06 station was 0.73 ± 0.03 ng/mL. Because 309 is the final point in the effluent stream, the concentration would be expected to be less than the concentration observed at X06. The sample for Outfall 309 was collected as the discharge entered White Oak Creek and probably represents a mixed source.

Fifth Creek receives effluents from several process wastes (300 Series Outfalls). Notably among potential mercury sources are the discharges from Buildings 4501 and 4505, which historically supported activities which utilized an amalgam process. Those discharge concentrations did not exceed the White Oak Creek background concentration of <0.5 ng/mL. Outfall 261 supposedly receives water from roof drains, spill areas, storage area drains, and cooling water discharges. Most of the discharge through Outfall 261 is from the Building 3500 environs. This outfall depicted the highest mercury concentration (4.77 ± 0.18 ng/mL) of all stations sampled in the scoping survey. A mercury spill (Table 1) is recorded from Building 3500 but quantitatively (<0.2 kg) is insignificant to the water concentration observed. Sources other than Building 3500 are suspected to contribute mercury through this outfall.

Table 7. Summary of analytical data (water)
for the 1987 scoping survey^a

Outfall number/location	n	ng/mL \pm 1 SE
<u>White Oak Creek</u>		
106	3	<0.05
202	3	<0.50
203	3	<0.50
204	3	<0.50
207	3	<0.50
209	3	<0.50
210	3	<0.50
216	3	<0.50
217	3	<0.50
218	3	<0.50
222	3	<0.50
223	3	<0.50
230	3	<0.50
232	3	<0.50
233	3	<0.50
234	3	<0.50
243	3	<0.50
301	3	<0.50
302	3	<0.50
303	3	<0.50
304	3	<0.50
308	3	<0.50
309	3	2.27 \pm 0.38
310	3	<0.50
311	3	<0.50
312	3	<0.50
313	3	<0.50
314	3	<0.50
7500B	3	<0.50
Flume	3	<0.50
WOD	3	<0.50
X01	3	<0.50
X02	3	<0.50
X03	3	<0.50
X04	3	<0.50
X06	3	0.73 \pm 0.03
X07	3	<0.50

Table 7 (continued)

Outfall number/location	n	ng/mL \pm 1 SE
<u>First Creek</u>		
142	3	<0.50
143	3	<0.50
241	3	<0.50
243	3	<0.50
244	3	<0.50
247	3	<0.50
248	3	<0.50
341	3	<0.50
342	3	<0.50
243	3	<0.50
X12	3	<0.50
<u>Fifth Creek</u>		
161	3	<0.50
162	3	<0.50
165	3	<0.50
261	3	4.77 \pm 0.18
262	3	<0.50
268	3	<0.50
361	3	<0.50
362	3	<0.50
363	3	<0.50
364	3	<0.50
365	3	<0.50
366	3	<0.50
367	3	<0.50
368	3	<0.50
<u>Melton Branch</u>		
181	3	<0.50
281	3	<0.50
283	3	<0.50
381	3	<0.50
383	3	<0.50
384	3	<0.50
386	3	<0.50
X08	3	0.60 \pm 0.00

Table 7 (continued)

Outfall number/location	n	ng/mL \pm 1 SE
<u>Miscellaneous</u>		
White Oak Creek Headwaters	3	<0.50
White Oak Creek Lower Creek	3	<0.50
Melton Branch Headwaters	3	<0.50
Melton Branch Small Middle Branch	3	<0.50

^aData in boxes represent the most significant concentrations.

Melton Branch receives waste water from the High Flux Isotope Reactor complex and the Transuranic Processing Facility (7500 area). Serial Numbered Outfall X08 is the NPDES monitoring station for the various holding ponds, prior to discharge through Outfalls 381-386. The mercury concentration at X08 was 0.60 ng/mL or background.

7.2 SPRING SAMPLING 1988 (WATER)

In February of 1988, 61 stations were sampled for mercury concentrations. Each site consisted of three replications for a total of 183 samples (Table 8). The lower limit for data reported for this series of data is <0.1 ng/mL, in contrast to <0.5 ng/mL in 1987. The detection limit is a function of the aliquot volume utilized in the analyses and does not indicate a change in methodology. Only eight locations contained quantitative concentrations (mean \pm 1 SE). Among those outfalls, 309 was the highest with a mean concentration of 2.10 ± 0.06 ng/mL. That concentration is essentially the same as measured in the 1987 survey and suggests a uniform input. The second notable concentration (1.17 ± 0.03 ng/mL) was from Outfall 367. Outfall 367 discharges into Fifth Creek east of Building 3036, the Isotope Area Storage and Service Building.

Table 8. Summary of analytical data (water) for the February 1988 sampling effort^a

Outfall number	n	ng/mL \pm 1 SE
<u>White Oak Creek</u>		
106	3	<0.1
202	3	0.17 \pm 0.07
204	3	<0.1
207	3	0.17 \pm 0.03
210	3	<0.1
217	3	<0.1
218	3	<0.1
223	3	<0.1
230	3	<0.1
233	3	<0.1
234	3	<0.1
301	3	<0.1
302	3	<0.1
304	3	0.13 \pm 0.03
305	3	<0.1
309	3	2.10 \pm 0.06
310	3	<0.1
311	3	<0.1
312	3	<0.1
313	3	<0.1
314	3	<0.1
X01	3	<0.1
X02	3	<0.1
X04	3	0.5 \pm 0
X06	3	<0.1
X07	3	<0.1
Flume	3	0.4 \pm 0
7500B	3	0.2 \pm 0
WOD	3	<0.1
<u>Fifth Creek</u>		
161	3	<0.1
262	3	<0.1
265	3	<0.1
268	3	<0.1
363	3	0.17 \pm 0.07
365	3	<0.1
366	3	<0.1
367	3	1.17 \pm 0.03
368	3	<0.1

Table 8 (continued)

Outfall number	n	ng/mL \pm 1 SE
<u>First Creek</u>		
143	3	<0.1
247	3	<0.1
248	3	<0.1
341	3	0.5 \pm 0
342	3	<0.1
343	3	<0.1
X12	3	<0.1
<u>Melton Branch</u>		
181	3	0.13 \pm 0.03
281	3	<0.1
381	3	<0.1
382	3	<0.1
383	3	<0.1
384	3	<0.1
386	3	<0.1
X08	3	<0.1
X09	3	<0.1
<u>Miscellaneous</u>		
White Oak Creek Headwaters	3	<0.1
White Oak Creek Lower Creek	3	0.17 \pm 0.03
Melton Branch Headwaters	3	<0.1
Melton Branch Small Branch	3	<0.1
Melton Hill Dam Melton Branch	3	<0.1
X03 Northwest Tributary	3	<0.1

^aData in boxes represent the most significant concentrations.

7.3 FALL SAMPLING 1988 (WATER)

In October of 1988, 88 locations were sampled for mercury concentrations. Each site consisted of 3 replications for a total of 264 samples (Table 9). The detection limit reported for this data set was <0.05 ng/mL. Most of the data reported were quantitative (fewer $<$ values). Four locations were significant among the observations, with mercury concentrations >0.5 ng/mL. For example, Outfall 106 had an average concentration of 0.72 ± 0.03 ng/mL. This outfall enters White Oak Creek south of Building 4508, the Metals and Ceramics Laboratory, and 100 m east of the confluence with Fifth Creek. The discharge from this outfall is from the storm drain system along Southside Drive. Outfall 311 had a mean concentration of 0.70 ± 0.02 ng/mL. This outfall serves some process wastes from Building 4500S. Serial Numbered NPDES station X07 serves the Process Waste Treatment Plant (Building 3544). This facility potentially receives wastewater from the majority of the Laboratory's facilities, including Basins 3539 and 3540 and the 3524 Equalization Basin. Constituents that exceed discharge limits from the holding basins are transferred to the Process Waste Treatment Plant for treatment (rad reduction by clarifier and ionic exchange column and pH adjustment) prior to discharge into White Oak Creek. The mean mercury concentration was 0.70 ± 0.02 ng/mL during this sampling period. The highest mercury concentration noted was from Outfall 367 along Fifth Creek, near the Isotopes Area Storage and Service Building (3036), with a mean of 1.87 ± 0.17 ng/mL. That compares with the spring sample concentration of 1.17 ± 0.03 ng/mL.

The Tennessee state standard (0.05 ug/L) is four times more stringent than the Federal standard (0.2 ug/L) for mercury in water. Much of the water chemistry data in this report exceed the Federal standard, while nearly all data exceed the state standard. This is not an indication of mercury contamination. The stream headwaters (background) concentrations exceed the state limit. Both standards are derived from literature abstractions from effects studies and do not reflect the state-of-the-art capabilities of analytical equipment.

7.4 MERCURY CONCENTRATIONS IN ORNL STREAM SEDIMENTS

Twelve sites were selected for mercury analyses in sediments. These sites were selected from previous water chemistry data, personal interviews with persons having knowledge of mercury spills at ORNL, and locations of suspected depositions of mercury. In 1982, (Van Winkle et al.) reported mercury concentrations among sediments of New Hope Pond (Y-12) and East Fork Poplar Creek. Shacklette et al., in 1971 indicated that the average concentration of mercury in sediments for the eastern conterminous United States was 0.147 ug/g. Mercury concentrations in clayey sediments in Cherokee Lake of East Tennessee have been reported to range from 0.6 to 2.5 ug/g (Turner and Lindberg, 1978). These latter data represent depositions from a mercury cell chloralkali plant. The sediment data for ORNL streams are presented in Table 10 and are not intended to infer a dilution with distance from the ORNL complex. For sediment data to be comparable, all materials must be sieved, with stones and organic materials removed. This was not the procedure with the sediments collected in this report. In fact,

Table 9. Summary of analytical data (water)
for the October 1988 sampling effort^a

Outfall number/location	n	ng/mL \pm 1 SE
<u>Fifth Creek</u>		
161	3	1.10 \pm 0
162	3	0.10 \pm 0
163	3	0.10 \pm 0
164	3	0.13 \pm 0.03
261	3	0.17 \pm 0.07
262	3	<0.05
265	3	<0.05
268	3	<0.05
361	3	<0.05
362	3	<0.05
363	3	<0.05
364	3	0.10 \pm 0
365	3	0.10 \pm 0
367	3	1.87 \pm 0.17
368	3	<0.05
<u>First Creek</u>		
141	3	<0.05
142	3	<0.05
143	3	<0.05
241	3	0.10 \pm 0
243	3	0.10 \pm 0
244	3	0.10 \pm 0
246	3	0.10 \pm 0
247	3	0.20 \pm 0
248	3	0.20 \pm 0
341	3	0.23 \pm 0.03
342	3	0.10 \pm 0
343	3	<0.05
344	3	<0.05
X12	3	<0.05
<u>Melton Branch</u>		
181	3	<0.05
281	3	<0.05
283	3	<0.05
381	3	<0.05
382	3	<0.05
384	3	<0.05
386	3	<0.05
X08	3	<0.05

Table 9. (continued)

Outfall number/location	n	ng/mL \pm 1 SE
<u>Miscellaneous</u>		
X09	3	<0.05
White Oak Creek Headwaters	3	0.1 \pm 0
White Oak Creek Lower Creek	3	<0.05
Melton Branch Headwaters	3	<0.05
Melton Branch Small Middle Branch	3	<0.05
Melton Hill Dam Melton Branch	3	<0.05
<u>White Oak Creek</u>		
101	3	0.2 \pm 0 ^b
103	3	0.2 \pm 0
106	3	0.72 \pm 0.03
109	3	<0.05
116	3	0.10 \pm 0
202	3	0.20 \pm 0
204	3	0.20 \pm 0
206	3	0.20 \pm 0
207	3	0.17 \pm 0.03
208	3	0.20 \pm 0
209	3	0.20 \pm
210	3	0.10 \pm 0
216	3	<0.05
217	3	0.13 \pm 0.03
218	3	<0.05
222	3	0.13 \pm 0.03
223	3	0.10 \pm 0
230	3	0.10 \pm 0
232	3	0.10 \pm 0
233	3	0.10 \pm 0
234	3	0.10 \pm 0
301	3	0.10 \pm 0
302	3	0.30 \pm 0
303	3	0.27 \pm 0.03
304	3	0.17 \pm 0.03

Table 9. (continued)

Outfall number/location	n	ng/mL \pm 1 SE
305	3	0.30 \pm 0
306	3	0.20 \pm 0
307	3	0.10 \pm 0
308	3	0.10 \pm 0
309	3	0.10 \pm 0
310	3	0.20 \pm 0
311	3	0.70 \pm 0.02
312	3	0.10 \pm 0
313	3	0.20 \pm 0
314	3	0.13 \pm 0.03
7500B	3	0.10 \pm 0
FLUME	3	0.20 \pm 0
WOD	3	<0.05
X01	3	<0.05
X02	3	0.30 \pm 0
X03	3	0.30 \pm 0
X04	3	0.17 \pm 0.03
X06	3	0.23 \pm 0.03
X07	3	0.70 \pm 0.02
X11	3	0.30 \pm 0

^aData in boxes represent the most significant concentrations.

^b0 standard error indicates all three replications had the same concentration.

the data may be viewed as minimal since the samples were not fractionated, and a small stone in an analytical aliquot could have a significant dilution bias.

New Hope Pond was sampled (Van Winkle et al., 1984) from a 0 to 95 cm depth for total mercury analyses. The intent of the vertical profile was to determine whether mercury deposition had been a continuous pathway for accumulation or if there existed discrete periods (spikes) of deposition. The data revealed that mercury increased with depth (time), reaching a maximum concentration at a depth of 70 to 75 cm. The lower concentrations at 0-5 cm deep suggested a reduction in mercury deposition in recent years. East Fork Poplar Creek receives stream flow from New Hope Pond. Mercury concentrations for surface sediments ranged from 19 to 127 ug/g at 2.1 and 22.2 km downstream from New Hope Pond, respectively.

The data for ORNL streams range from background (0.13 \pm 0.02) in White Oak Creek Headwaters to a maximum of 4874 \pm 2556 ug/g below Outfall 261 into

Fifth Creek. A summary of spatial mercury contamination in sediments of ORNL streams is presented in Table 10 and Fig. 3. While some of these concentrations appear to be alarming, it must be cautioned that the potential source plume is probably 0.5 m wide at its maximum width and extends an estimated 1.5 m. As an example, the sediment plume from Outfall 261 is 1 m long and 20 cm wide. The samples were collected to 5 cm deep. Considering a sediment bulk density of 1.4 g/cm^3 and the average mercury concentration of 4874 $\mu\text{g/g}$, it is estimated that a maximum of 68 g of mercury may be present. The sediment analyses identify sources of mercury which likely contribute to elevated stream concentrations. Mercury input into streams increases during high rainfall runoff events (Van Winkle et al., 1984). The concentration (22.26 $\mu\text{g/g}$) observed near Outfall 309 most likely reflects input from the Central Research Complex, Building 4500, whereas the concentrations along Fifth Creek reflect past spills from the lithium isotope separation/uranium-thorium metal production processes. The highest concentration (4874 $\mu\text{g/g}$) from Outfall 261 indicates a source from Building 3500 or other nearby facilities. The concentration (2.69 $\mu\text{g/g}$) in Melton Branch before joining White Oak Creek suggests the Solid Waste Storage Area (SWSA) 5 as a potential source.

8.0 CONCLUSIONS AND RECOMMENDATIONS

The water chemistry data are supported by the sediment data in identifying sources of mercury to ORNL streams. The sediment analyses indicate surface (0-5 cm) contamination only. However, to ascertain whether input to these areas is continuous, depth (cores) profile analyses are recommended. In addition, core studies should be initiated along a horizontal dimension to define the configuration of the source plume (sediments) and to suggest possible remedial actions to reduce these sources of mercury.

Both water and sediment sampling should be continued to determine the success of any remedial action and to identify any new source, should one appear.

Table 10. Summary of mercury concentrations (ug/g)
in sediments from ORNL streams

Location	n	Concentration \pm 1 SE
White Oak Creek Headwaters	3	0.13 \pm 0.02
Fifth Creek Outfall 362 Box	3	21.10 \pm 7.57
Fifth Creek Below Outfall 362	3	67.53 \pm 26.78
Fifth Creek Near Outfall 261	3	4874 \pm 2556
White Oak Creek Upstream of Fifth Creek	3	5.39 \pm 0.70
White Oak Creek Near Outfall 309	3	22.20 \pm 6.17
Northwest Tributary Upstream First Creek	3	0.17 \pm 0.03
First Creek Upstream of Northwest Tributary	3	0.67 \pm 0.29
White Oak Creek Downstream First Creek	3	8.93 \pm 0.66
White Oak Creek Upstream Melton Branch	3	0.31 \pm 0.08
Melton Branch at MBR2 Weir	3	0.53 \pm 0.07
Melton Branch Upstream of White Oak Creek	3	2.73 \pm 0.34

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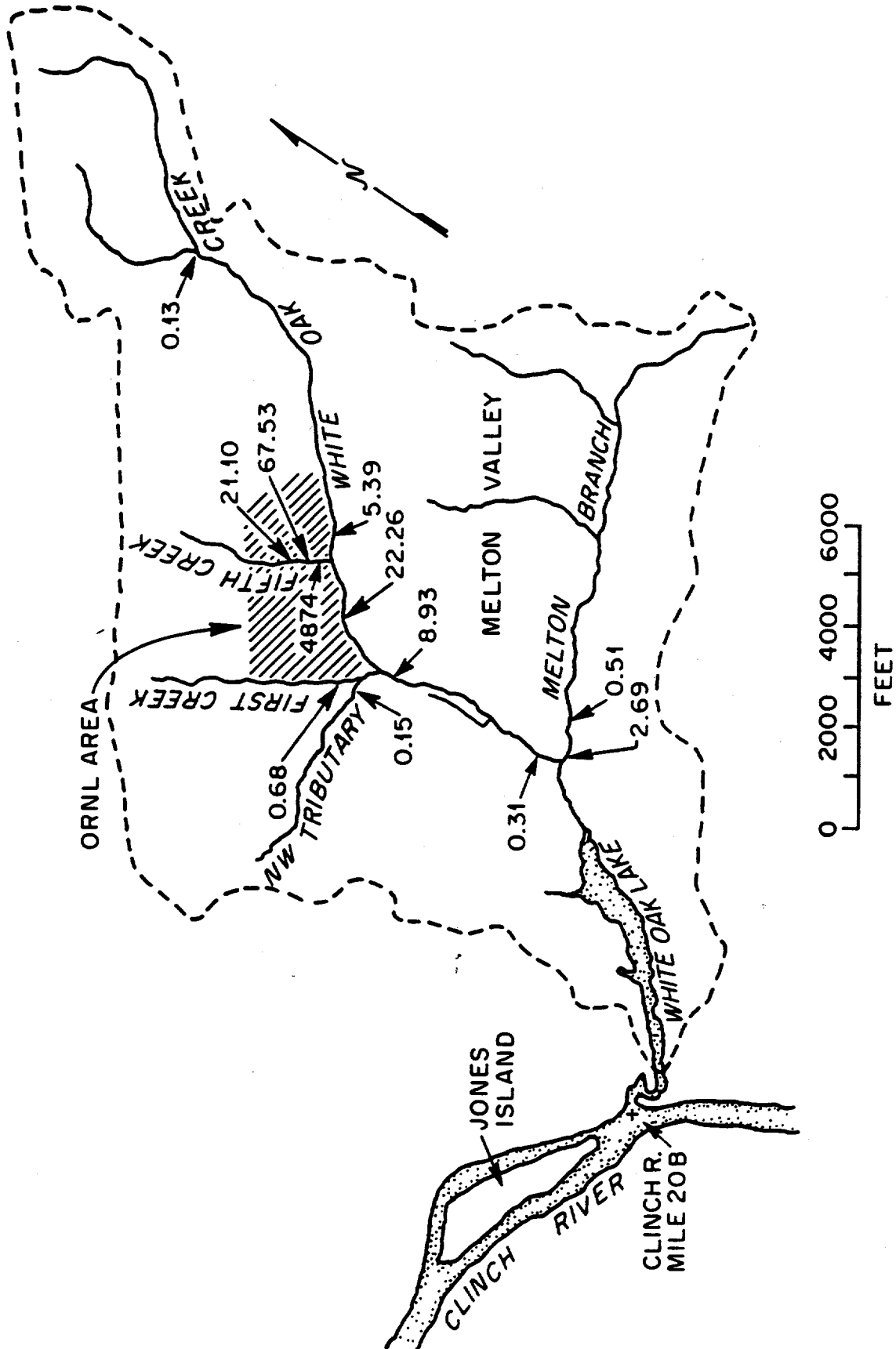


Fig. 3. Locations in ORNL streams with excess mercury concentrations in sediments. Statistics are summarized in Table 10.

9.0 REFERENCES

Personal communication, George B. Dinsmore to F. G. Taylor, October 1986, Oak Ridge National Laboratory.

Letter, B. M. Eisenhower to T. W. Oakes concerning mercury spill, Building 2525.

B. A. Kelly and B. M. Eisenhower, Spill Experiences at ORNL - 1978 to 1982, pp. 253-259, 1982 UCC-GAT Environmental Protection Seminar, Gatlinburg, Tennessee, April 5-7, 1982, CONF-820418.

Letter, T. W. Oakes to J. F. Wing, Department of Energy/Oak Ridge Operations, "Mercury in Soil and Sediment at ORNL," 1983a.

Letter, T. W. Oakes to J. F. Wing, Department of Energy/Oak Ridge Operations, "Mercury in Soil Samples at ORNL," 1983b.

Personal communication, George W. Parker to F. G. Taylor, October 1986, Oak Ridge National Laboratory.

H. T. Shacklette et al., "Mercury Content of Surficial Materials in the Conterminous United States," U.S. Geological Survey Circular 644: 1-5, 1971.

R. R. Turner and S. E. Lindberg, "Behavior and Transport of Mercury in a River-Reservoir System Downstream of an Inactive Chloralkali Plant," Environmental Science and Technology 12: 918-923 (1978).

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C., "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods," EPA-SW-846 (1982).

U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, Ohio, "Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79/020 (1983).

R. W. Van Winkle et al., Mercury Contamination in East Fork Poplar Creek and Bear Creek, ORNL/TM-8894, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory, 1984.

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